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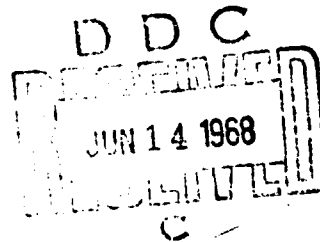## DDC AVAILABILITY NOTICE

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STUDIES ON FUMIGANT "ETHYLENE OXIDE" (I)

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Properties of Mixture of Ethylene Oxide and Methyl Bromide

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The limits of gaseous mixture of ethylene oxide and methyl bormide are measured. These findings indicate methyl bromide is effective as a diluent which narrows the inflammable range of gaseous ethylene oxide. Then the evaporating velosity of ethylene oxide and methyl bromide are compared as they evaporate from the mixture of these compounds.

This comparison shows the evaporating velosity of methyl bromide is slightly more rapid than that of ethylene oxide. This fact assures safety for the processes of fumigation.

The polymerization of ethylene oxide in the mixture of methyl bromide is investigated by means of heating. It is found as a result of this experiment that the addition of methyl bromide does not influence the polymerization of ethylene oxide.

The foregoing discussions lead to the conclusion that the mixture of ethylene oxide and methyl bromide have some excellent properties as a fumigant.

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Introduction

As is already known, ethylene oxide is synthesized in large quantities by air oxidation of ethylene from pyrolyses of naphta in petroleum chemistry, and is widely used in synthesis of the organic chemicals such as ethylene glycol and nonionic reagents. Ethylene oxide has also been known as a fumigant having high fungicidal and insecticidal effects and low boiling point. However, the experimental examples on this reagent as a fumigant are very few. The reason for this is that up to now, ethylene oxide is manufactured from ethylene obtained by dehydration of alcohol and results in a very high price. Another reason is that due to a wide explosive range in mixing with air, hazard is involved in using this reagent as a fumigant (during World War II, this reagent was used as a fumigant and a fire broke out in the warehouse).

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Recently as ethylene oxide is obtained in large quantities from petro-chemicals at a cheaper price, as mentioned above, the research on this reagent has reappeared. As noted in the literature, in order to narrow the explosive region, ethylene oxide is mixed with an inert reagent by making use of a good solubility of ethylene oxide in many chemical compounds. Thus, there were a method of adding equimolar sulfur dioxide [2,3,4] to this reagent and adding carbon dioxide [5] to this reagent. Also, there were the methods of using the mixture of ethylene oxide and methyl bromide [6] and the mixture of propylene oxide and dibromomethane [7] for the purpose of obtaining the balancing effect besides the improvement of physical properties. However, no attempt has been made to reduce the explosive properties by mxing ethylene oxide and halogen hydrocarbon. Therefore, the authors have used methyl bromide which has a comparatively high fungicidal and insecticidal effects and investigated the physical and chemical properties of the mixture systems. The interesting results are obtained from these investigations and reported in this paper.

II. A comparison of the physical and chemical properties of ethylene oxide and methyl bromide.

The physical constants of ethylene oxide and methyl bromide are compared and shown in Table 1.

Table 1

Comparison of Physical Constants of Ethylene Oxide and Methyl Bromide

	(1) 酸化エチレン	(2) 臭化メチル
(3)分　子　式	CH_2-CH_2 $\diagdown O \diagup$	CH_3Br
(4)分　子　量	44.05	94.95
(5)比　重 {液体 {気体	0.887D 1.53	1.732 3.28
(6)融　点	$-111.7°$	$-93.7°$
(7)沸　点	$10.7°$	$4.5°$
(8)溶解度 {水 {アルコール {エーテル	～ ～ 易	0.09 g/100g ～ ～
(9)以発限界 {上限 ▼ % {下限	100 3	14.5 13.5

LEGEND: 1. Ethylene oxide
           2. Methyl bromide
           3. Molecular formula
           4. Molecular weight
           5. Density   (solution
                          (vapor
           6. Melting point
           7. Boiling point
           8. Solubility   (water
                                (alcohol
                                (other   soluble
           9. Limit of explosion   (upper limit
                 ▼ %   (lower limit

From Table 1, an examination on the properties of both reagents
as a fumigant indicates the boiling point of ethylene oxide 10.7° and
methyl bromide 4.5°. When these are mixed, they are expected to evaporate
at the same time (see V). Also the density of gas is larger than air
for both. Ethylene oxide has a density of 1.53 times larger than air and
methyl bromide 3.28 times. Thus, the movement of gases during fumigation
is expected to be the same. As to the solubility in water, ethylene
oxide is completely soluble whereas methyl bromide is almost insoluble.
Generally, the solubility of fumigant in water is related to the humidity
in the fumigating system and the moisture content of the fumigating
material, and also influences the fungicidal and insecticidal effect, a
penetration to the fumigating material and chemical or physical
absorption on the fumigating material. The reports on this subject are
made by R. W. Kolbe, R. Schneiter [10] [11], S. Kaye, C. R. Phillips [12]
D. E. Munnecke, R. A. Ludwig, R. E. Sampson [13] [14], Kakuta, Tsuruta [15]
and Kakuta, Tobe [16]. Also, as mentioned previously, the explosive
region of two components system, the reagent and air, is 3-100% for
ethylene oxide and only 13.5-14.5% for methyl bromide. The explosion
limit of three components system, the fumigant mixtures and air, is
measured and the results are shown in III.

III. The limits of explosion of three components system, ethylene
oxide, methyl bromide and air.

The limits of explosion of three components system, ethylene oxide,
methyl bromide and air are determined by the following method.

Experimental apparatus and operation.

An apparatus shown in Figure 1 is constructed.

The explosion container of a glass tube with an inner diameter of
20 mm and a length of 250 mm is horizontally placed as shown in Figure 1
and a rubber stopper is put on both ends. A gas insertion tube and both
electrodes are inserted through the rubber stopper. The tip of an
electrode is connected with a manganin line of a diameter of 0.1 mm and
a length of 5 mm. This container is placed in an explosion proof steel
container with a glass window. After heating slightly the evaporating
container of ethylene oxide and methyl bromide, air is sent through
the pump. Thus, the predetermined gas mixtures of air, methyl bromide
and ethylene oxide are flowed into the explosion container at the rate
of 1.5-2 liters in one minute. At a minute or two after the flow rate
becomes constant, the inlet and outlet of the explosion container are
stopped with a pinchcock. After the gas flow has been stopped, the rubber
stopper on the outlet is loosened, and immediately 100 V of direct
current is passed from the distant spot. Manganin line is thus
disconnected with an electric spark and the presence of an explosion is
determined.

The experiment is repeated one to five times for one mixture ratio.

When there is an explosion, the rubber stopper flies apart with a severe sound. With no explosion, the Manganin line is just disconnected with an electric spark.

This method of measurements tends to narrow the limit of explosion as pointed out by Ryushyo [17].

For example:

a) In this experiment, the diameter of explosion container was 20 mm. With this tube diameter, the flame is cooled and its propagation is checked. Thus, with a larger tube diameter, the limit of explosion could be wider than the value of this measurement.

Figure 1
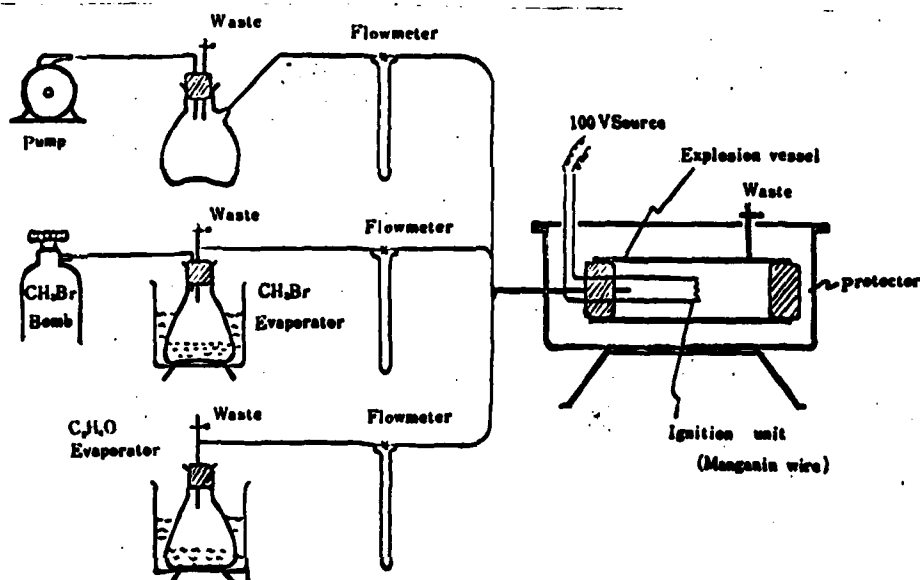
LEGEND: Apparatus for measuring the limit of explosion of three components system, methyl bromide, ethylene oxide and air.

b) The limit of explosion is wider when the flame is propagated upward by placing the container vertically and the flame source at the bottom rather than the horizontal propagation by placing the container horizontally as in this experiment.

Also a certain difficulty was encountered in regulating the amount
of gas flow in this experiment. However, near the limit line of explosion,
a number of experiments are conducted and the percentage of occurred
explosions is evaluated. The explosion percentages of 100%, 70-99%,
40-69%, 10-39% and 0% are recorded respectively.

The results of the measurements and observations.

Experiments are conducted on the mixture ratioes of 21 points and
the results are shown in Figure 2.

As is clear from Figure 2, the presence of methyl bromide makes
it possible to narrow the explosive region of ethylene oxide and air
mixture. Methyl bromide is, thus, effective in reducing the flammability
and explosion of ethylene oxide.

Many attempts have been made to narrow the limit of the explosion
by mixing inert gas to an explosive gas such as ethylene oxide. L. G.
Hess and V. Tilton have measured the limit of explosions by using nitrogen,
carbon dioxide and methane as diluents. When ethylene oxide is used as
a fumigant, it is a necessary condition to narrow the limit of the
explosion and handle it safely. It is preferable that the inert gas added
for this purpose also has an insecticidal effect.

Figure 2
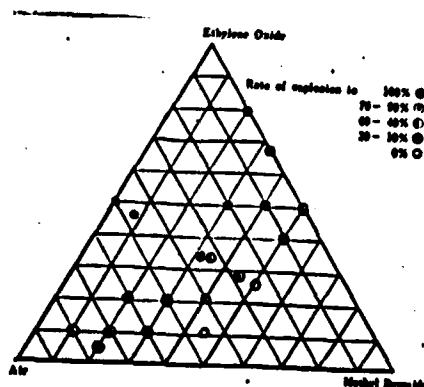
LEGEND: Limit of explosion of three components system, methyl
bromide, ethylene oxide and air.

The inert gases such as nitrogen and carbon dioxide are not
suitable from this standpoint. The mixture of ethylene oxide and carbon
dioxide was noted [5] to have a balancing effect but this seems to have a
certain limitation.

Methyl bromide discussed above is not only inflammable but also an effective insecticide, and is a valuable diluent for the fumigant. Therefore, the authors investigated further on the various properties of these mixture systems.

IV Average molecular weight, boiling point and solution density of mixture system.

The calculated values of average molecular weight and boiling point of ethylene oxide and methyl bromide mixture and the density at 0° are shown in Table 2. The boiling point is calculated based on the completely miscible ideal two components system. The density is measured with JIS float.

Table 2

Average Molecular Weight, Boiling Point
and Solution Density of Mixture System

(1)混合系の重量比	(倍化エチレン	0	25	33.3	50	75	100
	臭化メチル	100	75	66.6	50	25	0
(2) 平 均 分 子 量		94.95	82.1	77.9	69.5	46.7	44.05
(3) 沸 点 (°C)		3.5	4.6	5.0	5.95	7.8	10.7
(4) 液 比 重 (0°C)		1.732	1.400	1.319	1.185	1.032	D_4^7 0.887

LEGEND: 1. Weight ratio of mixture system (ethylene oxide
(methyl bromide

2. Average molecular weight
3. Boiling point (°C)
4. Solution density (0°C)

V. Examination on the evaporation of mixture system.

A consideration of ethylene oxide explosion in a warehouse requires that the boiling point of inert gas mixture should be similar to or slightly lower than that of ethylene oxide. If the boiling point of the inert reagent is higher, ethylene oxide reaches the explosive region before the inert reagent has evaporated from the system. On the other hand, if a low boiling inert reagent is used, the fumigant has to be placed in a high pressure container and is inconvenient for handling. Authors, therefore, conducted an experiment on the evaporating velocity of ethylene oxide and methyl bromide. The results are shown in Table 3. In this experiment, both fumigants, ethylene oxide and methyl bromide, are mixed at below freezing point and left at room temperature. After a certain amount has evaporated, the density of the remainder is measured at 0° and the weight ratio is evaluated from the density of

Table 2.

The composition of solution is 72 weight percent of methyl bromide and 28 weight percent of ethylene oxide.

As is clear from Table 3, the more the solution evaporates, the smaller the density of the remainder is. The concentration of ethylene oxide increases, i.e. the evaporation of methyl bromide is intense but not significantly so. A faster evaporation of inflammable methyl bromide than the flammable ethylene oxide is preferable from the safety standpoint.

Table 3

Experiment on the Evaporation of Mixture System

(1) 放置時間 (hr)	残(2)量		温(3)度		(4)比重	残流組合比(5)	
	ml	v %	(a)外温	(b)液温	(0°C)	臭a化メチル (wt %)	化エチレン (b) (wt %)
0	860	100	22	8	1.384	72	28
1.5	645	75	23	10	1.376	71	29
2.75	430	50	23	10	1.354	69.5	30.5
5.30	250	29	19	7	—	—	—
6.75	215	25	19	8	1.324	67.0	33.0
13.30	60	7	18	10	1.266	60.0	40.0

LEGEND: 1. Time left (hr)
2. Amount remaining
3. Temperature (a. outside temperature
(b. solution temperature
4. Density (0°C)
5. Mixture ratio of remainder (a. methyl bromide (wt %)
(b. ethylene oxide (wt %)

IV. Examination on thermal stability of mixture system.

Since ethylene oxide is readily polymerized on addition of a certain chemical compound and looses its effectiveness, a consideration on this point is necessary in selecting a mixture reagent. Authors have investigated the polymerization rate of ethylene oxide and methyl bromide mixture system by adding various kinds of metal and heating for a certain time. The results are shown in Table 4.

In this experiment, ethylene oxide and methyl bromide mixtures are placed in ampoules and sealed after putting the various kinds of metal in. These ampoules are placed in water kettle and heated at the bottom. After heating for 3 hours at 100°, these are taken out and cooled to room temperature.

Table 4

Polymerization Rate of Ethylene Oxide When Metal Is Added
to Ethylene Oxide, Methyl Bromide and these Mixtures
and after Heating at 100°C. (Ratio of Remainder)

No.	(1) 添加金属	(2) 供　試　液	(3) 加熱条件	(4) (a) 重　量（g）	(b) 酸化エチレンに対する重量比（%）
1 (5) スズ	臭化メチル+酸化エチレン 9.1g	(15) 加熱温度	0.0032	0.035
2 (6) 亜鉛	〃 8.2g	93～97°	0.0022	0.023
3 (7) スズメッキ	〃 9.3g	(16) 加熱時間	0.0027	0.029
4 (8) 鉄粉	〃 8.9g	3時間	0.1676	1.89
5 (9) ナシ	(13) 〃 8.5g	(17)	0.0029	0.034
6 (10) ナシ	臭化メチルのみ 9.0g	加熱せず	0.0002	0
7 (11) ナシ	酸化エチレンのみ 7.3g	加熱せず (18)	0.0040	0.055

(12)

(14)

LEGEND:
1. Added metal
2. Test solution
3. Heating condition
4. Remainder after evaporation (weight (g)
   (weight ratio of
   (ethylene oxide (%)
5. Tin
6. Zinc
7. Tin plating
8. Iron powder
9. None
10. None
11. None
12. Methyl bromide and ethylene oxide
13. Methyl bromide only
14. Ethylene oxide only
15. Heating temperature
16. Heating temperature
17. No heating
18. No heating

After cooling in ice water, the mouth of the ampoule is opened
and the content is transferred to a preweighed bottle. These are left
in a sulfuric acid desiccator until the weight of the content becomes
constant (the cover of the desiccator is for vacuum desiccator and the
stopcock is left open). The weight ratio of ethylene oxide is calculated
by the following equation [19].

(Ethylene oxide weight ratio)

$$= \frac{\text{(Weight of remainder after evaporation)}}{\text{(Weight of ethylene oxide in the material)}} \times 100$$

As is clear from Table 4, the polymerization of ethylene oxide itself is not promoted by adding methyl bromide to ethylene oxide. The effects of added metal are clearly noted and the presence of iron promotes the polymerization of ethylene oxide. Tin and zinc do not affect this reaction. The authors have measured the polymerization rate under the condition of No 5 (in Table 4) after 18 hours, 42 hours and 66 hours heating and no changes are observed. Thus, the prolonged preservation of this mixture system appears to be possible.

VII Summary.

Although ethylene oxide has long been known as an effective fungicidal and low boiling fumigant, use of this reagent alone is hazardous to the wide explosive region of two components system, air and ethylene oxide. In order to improve this, methyl bromide, which has the properties comparable to ethylene oxide and a high value as a fumigant, is mixed with ethylene oxide, and an experiment on their explosive properties is conducted. As a result, we observed that methyl bromide narrowed the limit of explosion of ethylene oxide.

Next, an experiment on the evaporation of ethylene oxide and methyl bromide mixture is conducted. Evaporation of inflammable methyl bromide is slightly faster than that of flammable ethylene oxide and the danger of filling the system with an explosive atmosphere of ethylene oxide, before the evaporation of inflammable reagent, is eliminated.

Also, the polymerization of ethylene oxide is very much accelerated by addition of a certain type of chemical compound, and ethylene oxide loses its function. The addition of methyl bromide does not affect this reaction at all.

From the above, ethylene oxide and methyl bromide mixture system is considered to have the superior properties as a fumigant. We are further investigating the fumigating effects of these mixture systems.

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